In the complex case, where the distribution of velocity is a simple vortex superposed upon solid rotation, the angle of convergence of the horizontal projection of the spiral paths cannot be constant over the whole area unless air is removed over the whole area. The relation vr = constant is the only one which is consistent with air passing horizontally across the area, with no extraction vertically except at the centre.

In all that precedes, the centre of the two-dimensional whirl has been assumed at rest. If the whirl is given a uniform velocity of translation, U, the distribution of velocity relative to the centre remains unaltered, and the spiral paths of instantaneous flow relative to the centre of the whirl are unaltered. All that is necessary is to add a correcting term, $-2\omega \sin \phi \,.\, \mathrm{U}y$ to the equation (21) for the distribution of pressure.

Some Experiments on the Catalytic Reduction of Ethylene to Ethane.

By Dorothy Muriel Palmer, Girton College, Cambridge, and William George Palmer, St. John's College, Cambridge.

(Communicated by Sir Wm. Pope, F.R.S. Received April 14, 1921.)

Finely divided reduced nickel has been applied as an active agent in the catalysis of a great range of reactions, but very little is known about the mechanism of its action. It was thought that the intensive study of some particular process might be of interest, in view of the paucity of quantitative information about catalysis.

The reaction selected for investigation was the combination of ethylene and hydrogen to form ethane. Sabatier* states that in the presence of freshly reduced nickel this reaction begins at 30°–45° C., and continues with the evolution of heat; thus there are few of the difficulties encountered when working at higher temperatures. Ethylene and hydrogen can both be obtained in a high degree of purity, and since the reacting and resultant substances are gases with simple volume relations between them, it was found possible to watch the progress of the reaction by a static method.

This was done by observing the pressure changes produced in a closed vessel containing the catalyst, together with a mixture of ethylene and hydrogen of known composition.

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* 'Comptes Rendus,' vol. 124, p. 1360.

The reaction chamber was a glass tube, heated electrically. It contained a glass ball which could be caused to roll from end to end of the tube by tilting the latter automatically at intervals, by this means an intimate mixture of the reacting gases was secured during the whole progress of the reaction. Unfortunately, this arrangement gradually forced the whole of the catalytic powder to the ends of the tube. In the series of experiments here described the catalyst was deposited on pellets of China clay, which were themselves, in the place of the glass ball, used to stir the gases. One end of the tube was sealed, the other was closed by a glass tap leading through a T-piece to a manometer, a gas reservoir, and a Fleuss pump, all isolated by suitable taps.

In the gas reservoir was a mixture of equal volumes of ethylene and hydrogen. The action takes place in accordance with the equation

$$C_2H_4 + H_2 = C_2H_6,$$

so that two volumes of such a gas mixture give one volume of ethane. The relative proportions of the gases in the reaction tube were kept constant by introducing this equal-volume mixture from the reservoir as fast as contraction took place. The total pressure inside the tube was thus maintained at a constant value; and a comparison of the rates of reaction was obtained by noting the rates at which it was necessary to pass gas mixture from the reservoir into the tube in order to keep the pressure constant.

The volume passed per minute was taken as the rate of the reaction. The rates so obtained were plotted against the times in minutes from the first observation, which was as soon as possible after the introduction of the gas mixture into the reaction tube, but not exactly the moment of introduction.

Two series of results were obtained. In one the temperature was nearly constant, the percentage of ethylene varying; in the other the temperature varied, but the reacting-mixture always contained equal volumes of the two gases. The limits of temperature within which observations were possible were 75°–120° C. The curve produced was always of the same form, showing a preliminary period in which the rate was negligible, then a very rapid increase in the rate to a maximum value, followed by a more gradual decrease. The position and height of the peak portion of the curve depended partly on the temperature and partly on the composition of the gas mixture.

The variations in temperature and composition were, of set purpose, made in haphazard order, and it was found that any curve could be repeated, even after a lapse of several weeks.

The results obtained with nickel powder and with the impregnated China clay pellets were similar, but the determinations with the powder were made with apparatus of a cruder form than that finally adopted; the curves are, therefore, not shown on the appended diagram. It is certain, however, that the China clay of the pellets played no part as catalyst.

Control experiments were performed with pure hydrogen and pure ethylene in the reaction tube. With ethylene there was no absorption whatever, but with hydrogen there was a small constant absorption, unchanged in rate after 2½ hours.

Preparation of the Catalyst and Reacting Gases.

Pure nickel oxide was prepared as follows. Sheet nickel was cleaned, then dissolved in pure dilute nitric acid. To this solution a slight excess of ammonia was added, the mixture was then boiled and filtered, to remove a small deposit of iron hydroxide. After a repetition of this process, there was no further formation of precipitate. The solution was then condensed, and excess of concentrated ammonia solution was added. Light violet crystals of a nickel-ammonia complex formed, were filtered off, and washed with concentrated ammonia. On boiling with much water, these crystals decomposed, precipitating a bright green hydroxide of nickel in a powdery form. This was collected, washed and dried, and, when needed, was dissolved in dilute pure nitric acid.

Cylindrical rods of china clay, of diameter 3 mm., were used as support for the catalyst. The composition of these rods was as follows :—

	Per cent.		Per cent.
SiO_2 =	65·27	CaO =	0·43
Al_2O_3 =	30·06	K_2O =	1·61
Fe_2O_3 =	0·65	Na_2O =	0·723
MgO =	0·173		

They were rendered inactive as catalysts by ignition to bright redness for four hours. Two or three of these rods were broken into short lengths, then soaked and boiled in the liquid obtained by concentrating the solution of the purified nickel hydroxide. The pellets were dried at 100° C., then gently ignited, shaken free of loose powder, and placed in the reaction tube. The deposit of nickel oxide was reduced by the passage through the tube of dry electrolytic hydrogen. At the temperature employed, 300° C., this reduction was very slow, and it was several days before water could no longer be detected in the issuing gases. The pellets were then allowed to cool in an atmosphere of hydrogen. No air was ever admitted into the reaction tube. The exit was sealed off when the reduction of the nickel was complete.

The total quantity of nickel in the reaction tube was estimated electrolytically at the end of the series of readings. Its quantity was found to be 0·068 grm.

Ethylene was prepared by the action of zinc-copper couple on freshly distilled ethylene dibromide, boiling at 131° C. The gas was washed by being bubbled through tubes containing more of the couple immersed in alcohol. A gas analysis by Hempel's method, using bromine water, indicated an ethylene-content of over 99 per cent.; but, in order to remove any possible traces of air or hydrogen, the ethylene was solidified by cooling in liquid air, and then fractionated. It was stored in an aspirator over water saturated with pure ethylene.

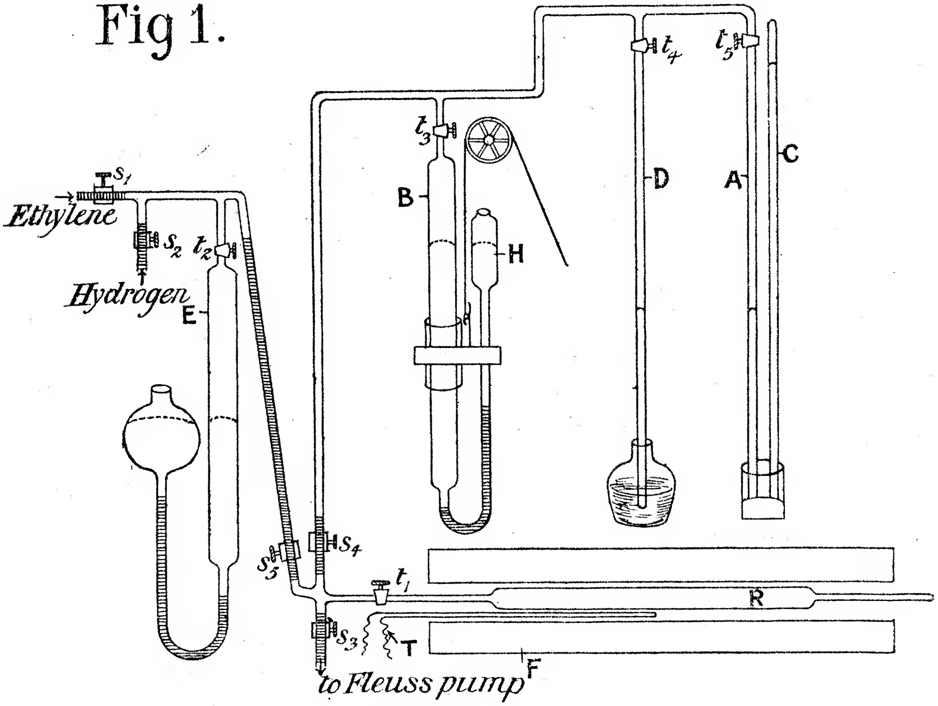
Hydrogen was prepared by the electrolysis of caustic potash, as described by one of us.* It also was stored over water.

When required, these gases were drawn through trains of soda-lime and calcium chloride tubes into the mixing vessel.

Apparatus.

The furnace, F, was especially constructed, so that the heating might be as even as possible throughout the cavity. The inner tube of brass was wrapped in asbestos paper, then evenly wound with a heating coil of constantan wire. This was insulated with asbestos cord, then the whole was packed in a cylindrical iron case filled with ignited magnesia. The furnace was supported

Fig 1.



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* 'J. Soc. Chem. Ind.,' vol. 39 (20), 316T.

at its middle point, so that it was free to turn in a vertical plane, and could be rocked up and down, either by hand or by an electric motor. The temperature inside the brass tube was read by means of an insulated thermocouple, T, with its hot junction placed at the middle of the tube, and its cold junction in a Dewar flask filled with melting ice (see fig. 1).

The capacity of the reaction tube, R, was about 70 c.c. Its length was 30 cm., and its inside diameter 1·7 cm. The length was several inches less than that of the furnace, that there might be no cooling effect at the ends. When the prepared pellets had been placed inside, the ends of the tube were drawn out and fused to pieces of capillary tubing. The exit was sealed off after the reduction of the nickel was complete, and the entrance was closed by a glass tap, t_1. The volume of gas in these capillary end pieces was negligible. Asbestos wool was used to pack the glass reaction tube securely into the heating tube; this also prevented the entrance of air currents.

A plan of the apparatus is shown in the diagram. The shaded portions of the connections were made of rubber pressure tubing, the rest was glass; glass could not be used throughout, as flexible connections were necessary, to allow for the motion of the furnace. The taps t_1, etc., were of glass, those marked s were ordinary screw clips.

E, a gas burette filled with mercury, was used for the preparation of the required mixture of dried gases. A was a manometer dipping into mercury with an ordinary barometer C at its side. D was a water manometer, to read small alterations of pressure. It was isolated by the tap t_4 with capillary tubing on either side of it. As t_4 was opened only when the pressures on either side were approximately equal, there could be no appreciable escape of water vapour into the rest of the apparatus. Millimetre scales were fixed behind A, C and D.

B, a glass measuring tube graduated in tenths of a cubic centimetre, was filled with a mixture of equal volumes of ethylene and hydrogen. A small pulley and windlass allowed a very gradual raising of the mercury reservoir H; thus, the taps t_1, t_3, t_4 and s_4 being open, the liquid in D could be kept at a constant level by an adjustment of the height of H.

Procedure.

The furnace was heated overnight, to secure equilibrium of temperature inside the reaction tube. That constancy of temperature could be obtained was shown by a blank experiment with nitrogen in R. When the taps t_1, t_3, t_4, t_5 and s_4 were open, the liquid in D showed only small oscillations during a four-hour period of observation. B was filled with its equal volume mixture, and the gas mixture to be investigated was prepared in E.

The taps s_1, s_2, t_2, t_3, t_4, were closed, the others opened, and the apparatus was exhausted by means of a Fleuss pump, to a pressure of 3 mm. of mercury. The tap s_3 was closed, t_2 opened momentarily, then reclosed, and the exhaustion was repeated. After a repetition of this washing process, the gas mixture from E was allowed to flow into the rest of the apparatus, t_3, t_4 and s_3 being closed, until the mercury height in A showed that the pressure throughout was nearly atmospheric, and approximately equal to that of the reserve gas in B. Finally t_3 and t_4 were opened; the pressure throughout rapidly attained equilibrium, t_2 was closed, and simultaneous readings were taken of the time and the heights of the liquids in D and B. t_1 was now closed, and the furnace was slowly rocked, at that rate which just allowed the catalytic pellets to roll from one end of R to the other between each reversal of position. This ensured a constant stirring of the gases in R—without this, the measurements recorded would be observations of gaseous diffusion, not of the rate of reaction.

While t_1 was closed, gas was slowly absorbed by the pressure tubing—this was counteracted by a raising of H sufficient to keep the water-level in D constant. After half-an-hour this absorption became negligible, and was always negligible in comparison with the absorption due to reaction between the gases at periods when the rate of combination was rapid. After a suitable interval, varying from one to ten minutes, the readings of the time and of B were noted, t_1 was opened and H rapidly adjusted to restore the constant pressure level in D. The new reading of B was observed, and t_1 was closed. These readings were repeated at intervals depending on the rate of reaction. During the "peak" portion of the reaction curve, the tap t_1 was left open all the time, as H had to be raised very rapidly and continuously. The reaction could not be followed beyond 120° C., the rate of absorption becoming too great to be measured by this apparatus.

Exhaustion of the reaction tube between successive experiments was the only revivification process employed. No diminution in catalytic activity was observed after three months of intermittent use.

Discussion of Results.

The curve showing change of reaction-velocity with time at constant temperature is of an unexpected form and presents some unusual features.

In most of our experiments there was a period, varying in duration from three hours to a few seconds after the mixed gases had been brought into contact with the nickel, during which time practically no reduction in volume, and therefore no hydrogenation, took place. This "induction" period was followed by a very rapid increase in reaction-velocity to a sharp maximum.

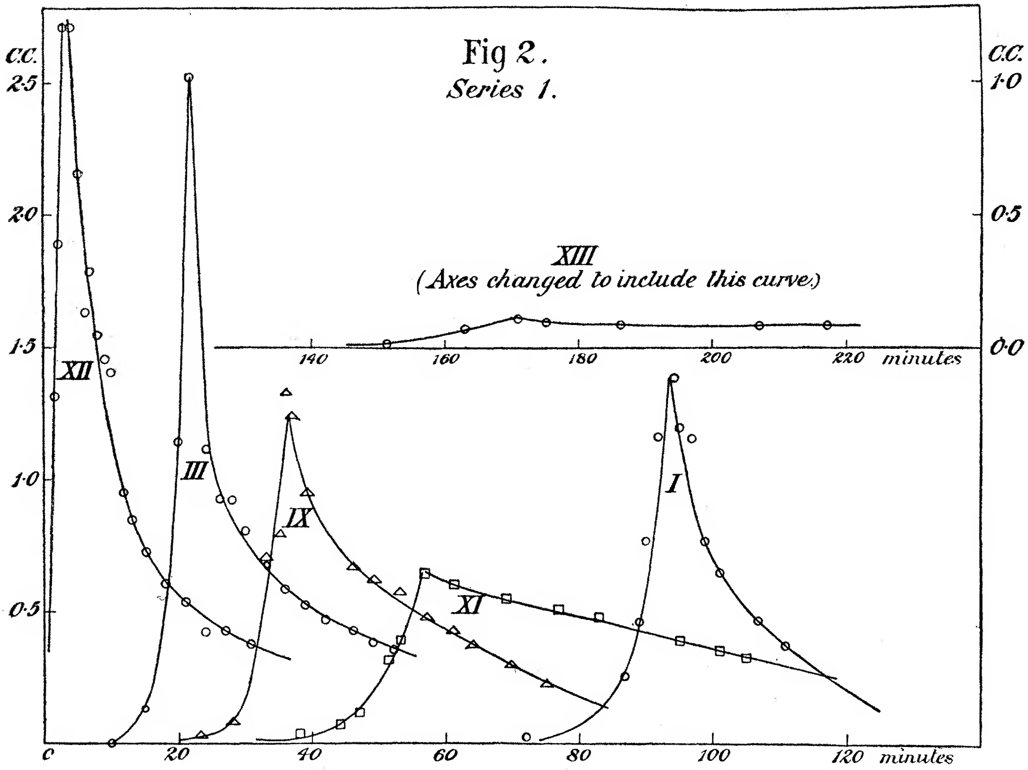
Series I.—Composition of Gas Mixture Constant, Temperature varying.

No. of expt.	II.		XIII.		XI.		I.		IX.		III.		XII.	
Temperature.	73° C.		81° C.		86 ·5° C.		98° C.		102° C.		103° C.		119° C.	
Per cent. C_2H_4.	50 ·5 per cent.		50 ·9 per cent.		50 ·9 per cent.		50 ·0 per cent.		50 ·0 per cent.		50 ·5 per cent.		50 ·7 per cent.	
	Time in mins.	Rate.	Time.	Rate.	Time.	Rate.	Time.	Rate.	Time.	Rate.	Time.	Rate.	Time.	Rate.
	Six hours.	No absorption observed.	0–141	No action	23	0 ·01	0– 52	No action	23	0 ·03	10	0 ·054	1½	1 ·31
			151	0 ·01	38	0 ·04	62	0 ·02	28	0 ·08	15	0 ·13	2	1 ·87
			163	0 ·06	44	0 ·08	72	0 ·03	33	0 ·69	20	1 ·14	3	2 ·71
			171	0 ·10	47	0 ·12	82	0 ·06	35	0 ·79	22	2 ·52	4	2 ·71
			175	0 ·09	51	0 ·32	87	0 ·26	36	1 ·33	24	1 ·11	5	2 ·15
			186	0 ·08	53	0 ·39	90	0 ·76	37	1 ·24	26	0 ·92	6	1 ·63
			207	0 ·08	57	0 ·64	92	1 ·16	39	0 ·95	28	0 ·92	7	1 ·78
			217	0 ·09	62	0 ·60	95	1 ·19	43	0 ·76	30	0 ·80	8	1 ·54
					69	0 ·55	97	1 ·15	46	0 ·67	33	0 ·67	9	1 ·45
					77	0 ·51	99	0 ·75	49	0 ·62	36	0 ·58	10	1 ·40
					83	0 ·48	101	0 ·64	53	0 ·57	39	0 ·52	12	0 ·94
					89	0 ·46	107	0 ·46	57	0 ·48	42	0 ·46	13	0 ·84
					95	0 ·39	111	0 ·38	61	0 ·43	46	0 ·42	15	0 ·72
					101	0 ·35	—	—	64	0 ·38	49	0 ·37	18	0 ·59
					105	0 ·32	—	—	70	0 ·31	52	0 ·35	21	0 ·53
									75	0 ·24	—	—	24	0 ·42
													27	0 ·42
													31	0 ·37

NOTE.—The "induction period" in Experiment XI is abnormally brief, probably owing to an incomplete removal of the reaction products of the preceding experiment.

Fig 2.

Series 1.



Finally, the rate of reaction fell rapidly away from this maximum to a nearly steady value.

The initial period of inactivity might possibly be due to the selective adsorption of oxygen contaminating the electrolytic hydrogen. This oxygen would be gradually removed by combustion with hydrogen or ethylene.

Such an explanation would require the duration of the "induction" period at a given temperature to be approximately proportional to the hydrogen-content of the gas mixture, which an inspection of the series of results for different gas mixtures at 104° shows not to be the case:—

Temperature 104° C.

Duration of induction period in minutes.	Percentage by volume of hydrogen in mixture.
150	75
40	65
22	50
Very short	35 25 15

Series II.—Composition of Gas Mixture varying, Temperature nearly Constant.

No. of experiment.	IV.		X.		III.		VI.		VII.		VIII.	
Temperature.	103·5° C.		105·5° C.		103° C.		105° C.		103° C.		103° C.	
Per cent. C_2H_4.	25·5 per cent.		35 per cent.		50·5 per cent.		65·2 per cent.		75 per cent.		85 per cent.	
	Time in minutes.	Rate.	Time.	Rate.	Time.	Rate.	Time.	Rate.	Time.	Rate.	Time.	Rate.
	0–108	No action	11	0·048	10	0·054	1	2·57	1	0·56	2	0·07
	118	0·018	21	0·04	15	0·13	2	2·11	$3\frac{1}{2}$	1·09	5	0·09
	138	0·03	36	0·12	20	1·14	3	1·93	5	1·85	7	0·29
	148	0·13	40	0·71	22	2·52	5	1·20	6	1·02	9	0·35
	150	0·23	41	1·47	24	1·11	7	0·87	7	0·83	11	0·37
	151	0·42	42	0·95	26	0·92	8	0·74	10	0·65	13	0·30
	154	0·33	44	0·71	28	0·92	10	0·64	12	0·46	15	0·30
	155	0·28	45	0·62	30	0·80	11	0·55	15	0·37	17	0·28
	157	0·23	47	0·57	33	0·67	14	0·46	18	0·28	19	0·21
	160	0·24	49	0·50	36	0·58	17	0·37	20	0·23	20	0·19
	162	0·23	53	0·45	39	0·52	20	0·28	26	0·15	25	0·18
	165	0·24	57	0·39	42	0·46	22	0·23	33	0·08	30	0·093
	169	0·28	61	0·34	46	0·42	23	0·18	38	0·07	35	0·074
	172	0·28	67	0·29	49	0·37	28	0·15	—	—	41	0·056
	175	0·28	74	0·24	52	0·35	46	0·032	—	—	46	0·037
	178	0·28	82	0·19								
	181	0·28	96	0·12								
	185	0·25	106	0·09								
	188	0·22										
	192	0·22										
	196	0·19										
	201	0·15										
	213	0·13										
	233	0·08										

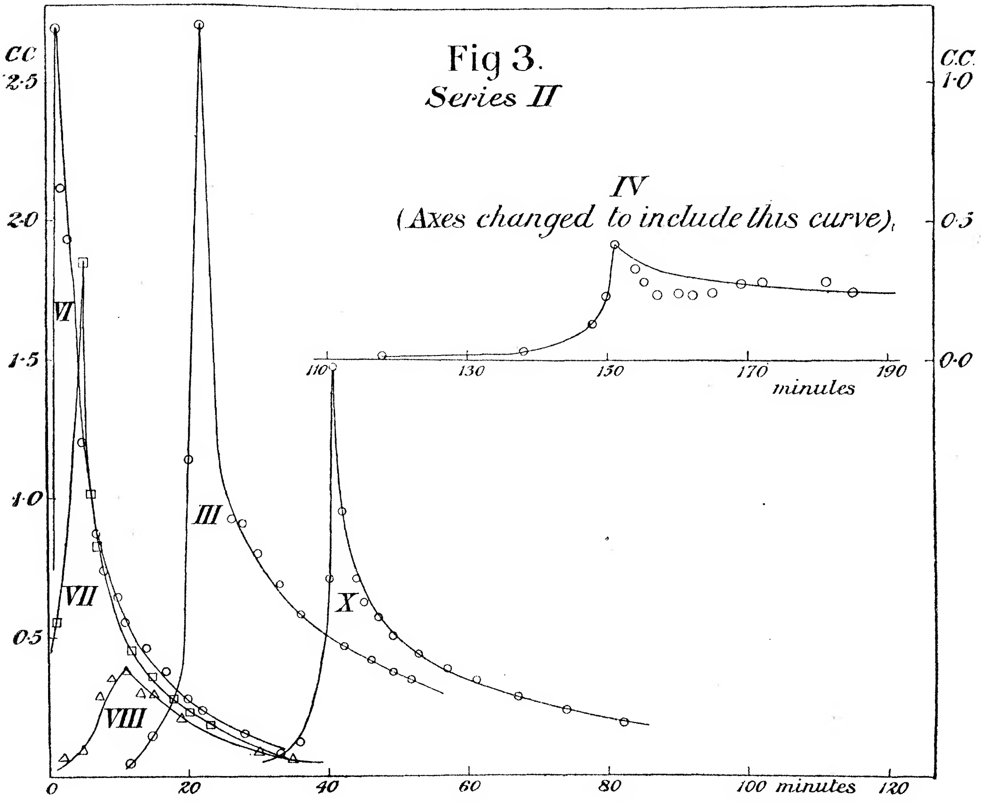


Fig 3.
Series II

A complete explanation of the form of the reaction-velocity-time curves can be put forward on the basis of the following assumptions:—

(*a*) Hydrogen is selectively adsorbed on nickel from mixtures of all the compositions studied.

(*b*) Ethylene is adsorbed only after activation (chiefly by thermal contact with a molecule undergoing hydrogenation).

On bringing the gas mixture into contact with the nickel, this becomes at once covered almost completely with hydrogen, only a few ethylene molecules being present in the adsorption layer; reaction with the formation of ethane takes place with these and the adsorbed hydrogen. The heat liberated in the hydrogenation is at once communicated to the molecules surrounding the hydrogenated molecule, leading to volatilisation of hydrogen and activation, followed by condensation, of ethylene.

The relative amounts of hydrogen and ethylene adhering to the surface of the catalyst thus change rapidly, once a number of centres of reaction have developed. This stage corresponds to the maximum in the reaction-velocity.

Finally, the catalyst becomes covered almost completely with ethylene, to the exclusion of hydrogen.

Hydrogenation thus takes place comparatively slowly by collision between adsorbed ethylene and hydrogen or by diffusion of hydrogen to the catalyst surface through a thin layer of ethylene.

It will be noticed that the "induction" period is reduced in a very marked way either by increase of ethylene-content in the gas mixture or by increase in temperature, while the rate of reaction after the maximum has been reached is only very slightly affected by temperature. These observations are in accordance with the above theory. The final rate of reaction falls off gradually, owing to the accumulation in the reaction tube of inert ethane which acts as a diluent to the gas mixture.

The Catalytic Activity of Copper.—Part II.

By William George Palmer, St. John's College, Cambridge.

(Communicated by Sir Wm. Pope, F.R.S. Received April 14, 1921.)

In Part I of this series of papers,* the writer described the construction of an apparatus for determining directly the relation between reaction-velocity and temperature in the catalytic dehydrogenation of ethyl alcohol by the action of copper produced from cupric oxide by reduction. Some preliminary results were also given. This work has now been extended both by using reducing agents other than hydrogen (namely, carbon monoxide and methyl alcohol vapour) in the preparation of the catalyst and by the use of other alcohols as reacting substances.

In the earlier work, the method consisted in obtaining an automatic record of the rate of escape of hydrogen liberated in the reaction, at several different temperatures, the temperature being kept constant during each experiment. This method proved very laborious, since only by making experiments at a great number of different temperatures could a sufficiently intimate knowledge of the influence of temperature be obtained. Also, the catalyst had always to be reprepared by oxidation and reduction between experiments.

It has now been found possible to obtain a continuous record of the change of activity, while the temperature of the reaction is gradually increasing through the range to be studied.

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* 'Roy. Soc. Proc.,' A, vol. 98, p. 13.